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Investigation of the Temperature Dependence of Free Volume in Polymethylpentene by Positron Annihilation Method

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Positron lifetime measurements in polymethylpentene were performed in a wide temperature range. A conventional fast–slow coincidence lifetime spectrometer with plastic scintillators was used. All the measurements were made in vacuum. Additional measurements (X-ray diffraction, differential scanning calorimetry, and mechanical spectroscopy) were also performed to establish properties of samples. Mean free volume radii in the investigated samples were estimated from the positron lifetimes measurements results. An increase in I_3 with the elapsed time of measurements was observed.

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1. Introduction

Positron annihilation spectroscopy turned out to be a very useful method for investigation of different aspects of polymer properties [1, 2]. Many different external conditions can perturb the fate of the positron in polymer matter and due to this, they might change its lifetime. In this paper we present results of the positron lifetime measurements in polymethylpentene –[–CH_2–CH–(CH_2–CH–($2CH_3$))–]–. This polymer is one of the polyolefines. It is a semi-crystalline polymer for which five modifications (designed I, II, III, IV, V) were found. The modification I is usually obtained when the sample is prepared by melt process. The other four modifications (II–V) might be prepared from diluted solutions. It is relatively easy to get the samples of different structures and we are going to study them in future. We presented very rough and preliminary results of our measurements in the same material in [3].

2. Experimental

A conventional slow–fast coincidence spectrometer with plastic scintillators was used. The time resolution of the spectrometer, approximated by two Gaussian curves, was determined by analysing the positron lifetimes in kapton foils. Typical values of the full widths at half of the maximum (FWHM_i) were: $\mathrm{FWHM}_1 = 258.4$ ps, ($I_1 = 73.58\%$); $\mathrm{FWHM}_2 = 365.9$ ps. Positron lifetime spectra were accumulated to approximately 0.26×10^6 counts. A positron source (^{22}Na, about 0.15 MBq) was sealed between two kapton foils. The source correction was taken into account during numerical evaluations. All of the measurements were performed in vacuum (about $10^{-8} \div 10^{-9}$ mbar at low temperature, and $10^{-4} \div 10^{-5}$ mbar, at room temperature). Dimensions of the cold head and its high vacuum jacket allowed us to install two scintillation detectors at the distance of about 25 mm. It reduced drastically the count rate. We acquired one spectrum, so as to reach the above-mentioned statistics, about 24 hours. A closed cycle helium refrigerator system was used to keep the sample at low temperatures. A digital, microprocessor controlled measurement and a control unit was used to regulate the temperature of the sample. It allowed one to keep the temperature of the sample constant, within $\pm(25 \div 30) \times 10^{-3}$ K. The temperature range of the measurements was from 8.3 K to 299 K. We started our measurements at 299 K and we cooled the sample down to 8.3 K and then we heated it up to 280 K. The measurements were carried out at 20 K spaced intervals (in the temperature range from 299 K to 200 K and from 120 K to 8.3 K) for the cooling cycle. The same temperature steps were used in the heating cycle (in the temperature range from 30 K to 110 K and from 210 K to 290 K). The measurements in the temperature range from 190 K to 120 K were performed at 10 K spaced intervals (during the cooling cycle). The same temperature intervals were used in the heating cycle (in the temperature range from 115 K to 205 K). Our choice of the temperature steps was selected so as to follow some changes in the temperature characteristics. The sample was kept in the newly chosen temperature for 40 to 50 min before we started the new measurement.

The sample was made of 0.5 mm thick film of polymethylpentene, from Goodfellow. Density of the sample material: 0.835 g cm^{-3}, hardness (Rockwell): R85, tensile modulus: 1.5 GPa, tensile strength: 25.5 MPa. Ten square shaped pieces (17×17 mm^2) of the polymethylpentene film were cut down from the polymer sheet and the positron source was sandwiched between them (five squares on each side of the source). The sample did not undergo any additional thermal treatment before the measurement.

Additional measurements were carried out on the sample material: the X-ray scattering diffraction pattern was recorded using the Philips diffractometer, thermal characterization of the samples by differential scanning calorimetry (DSC) was performed using Perkin Elmer DSC7 type and the first heating run (20 deg/min) was recorded (by comparison of the X-ray patterns of the studied

sample and the ones reported in [4], it was possible to assign the crystalline structure to the I modification), and dynamic mechanical thermal analysis (DMTA) was carried out with the same system as previously [5, 6] within a frequency range of 0.01–10 Hz.

3. Results and discussion

Positron lifetime measurements were performed on the polymethylpentene sample. The spectra were analysed using the package programs written by Kirkegaard et al. [7]. The total number of counts accumulated in our spectra was relatively small (0.26×10^6) and this was why we decided to analyse them in two-step process. As the first step of approximation two exponential components were fitted to the measured spectra with no constraints on lifetimes and intensities during numerical analysis. This procedure resulted in reasonable τ_2 and I_2 values. Nevertheless it is generally accepted to fit three or four components to the measured spectra for polymer samples. As statistics of the obtained spectra was low we decided to fit three components but a lifetime of one of them was fixed. We fixed the lifetime of the second component, τ_2. According to our former measurements we chose 380 ps for the fixed τ_2 value.

According to a model proposed by Tao [8] and Eldrup et al. [9], the longest lived component of the positron lifetime spectrum may be correlated with the mean radius of the free volume cavity in the polymer matter. They proposed a following equation:

$$\tau_3 = 0.5[1 - R/(R + 0.1656) + 1/(2\pi)\sin(2\pi R/(R + 0.1656))]^{-1}, \tag{1}$$

where τ_3 is the *o*-Ps lifetime expressed in nanoseconds, R is the mean radius of the spherical well expressed in nm and 0.1656 nm is an empirical constant.

The results of our measurements suggest that there is no correlation between the temperature and τ_1, and I_1 values. On the contrary, it seems that τ_3 and I_3 values show some tendencies with temperature. The value of the longest lived component, τ_3, vs. temperature is shown in Fig. 1. The τ_3 value decreases gradually with decreasing temperature, in the cooling cycle and increases in the heating cycle. It seems that there is no thermal hysteresis in the presented results. In spite of this, it seems that there is no simple correlation between the relative intensity of the longest lived component of the positron lifetimes, I_3, and temperature. The I_3 value as a function of temperature is presented in Fig. 2. It is absolutely clear that experimental points in the heating cycle do not follow the results observed in the cooling cycle. Going down from room to lower temperatures I_3 decreases first (to approximately 240 K) and then it starts to gradually increase (in both the cooling and the heating cycles). Finally, the I_3 value, starts to decrease (in the heating cycle) for temperatures higher than about 140 K.

Many authors observed a similar τ_3 behaviour vs. temperature as we did for different polymers: [10–13] (their data in dark, as we performed our experiments in dark as well).

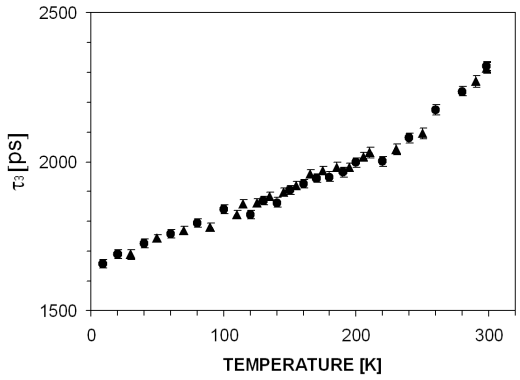

Fig. 1. τ_3 values vs. temperature: • — cooling cycle, ▲ — heating cycle.

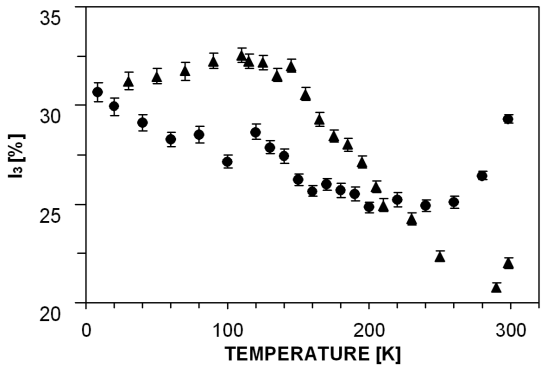

Fig. 2. I_3 values vs. temperature: • — cooling cycle, ▲ — heating cycle.

The relative intensity of the longest lived component, I_3, vs. temperature is more complex. It is well known and generally accepted that in a framework of the spur model of positron annihilation a large number of free electrons is produced in the sample irradiated by positrons. When a positron with a kinetic energy of several keV enters an absorber it quickly reaches thermal energies. It looses its energy mainly on exciting and ionisation of atoms and molecules of the absorber. The electrons released in this process might be trapped in shallow traps [14]. Free volume cavities may play a role of such traps in the polymer sample. During positron lifetime measurements in polymers, the number of electrons trapped in these traps increase, especially in low temperatures. In higher temperatures these electrons are detrapped. A similar explanation of the observed phenomena proposed Hirade et al. [15]. If it is so, the increasing number of the trapped electrons will cause the increase in the positronium formation probability. It might results in a larger value of I_3, during the heating cycle, from 8.3 K to about 140 K. For the higher temperatures I_3 starts to drop as the result of detrapping of the electrons. Figure 2 shows these changes.

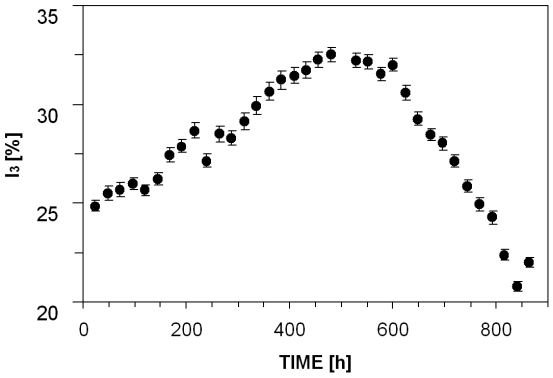

Fig. 3. I_3 values vs. elapsed time of the measurements.

From this figure one can find out that I_3 rises gradually with temperature from about 200 K to 8.3 K (in the cooling cycle) and it sill rises in the heating cycle from 8.3 K to about 150 K. Though the temperature of these measurements was not constant, it was obviously low. We tried to look for the tendency of the I_3 values changes with time. Our attempt is presented in Fig. 3. The time values, as an independent variable, was estimated taking into account the elapsed time of the measurements. The time started to run, in Fig. 3, when the temperature of the investigated sample was 200 K (in the cooling cycle) and it ran till the end of the measurements. It seems that I_3 rises with the measurements time (or with keeping the sample in temperature below 200 K). I_3 starts to decrease after about 600 hours of the measurements. After this time of the measurements the temperature of the sample reached about 150 K (in the heating cycle). The observed tendency of I_3 changes with time confirms the already mentioned mechanism of the formation of the electron traps in polymer in low temperature. The beginning of the decrease in the I_3 value at about 150 K might be explained as the result of detrapping of electrons from their shallow traps, due to molecular motion of the polymer molecules, which results in decreasing of the *ortho*-Ps formation probability. Quite similar behaviour of I_3 with time, in low but constant temperature, was observed by Chen et al. [11] and by He et al. [13] (data for the measurements in dark again).

4. Conclusions

In conclusion, we present the results of the positron lifetime measurements in polymethylpentene. At low temperature we observed the effect of trapping of the free electrons produced during positron irradiation. These electrons are trapped in free volume cavities resulting in the increase in the *o*-Ps formation probability. For the temperatures higher than about 150 K, these electrons are detrapped and relative intensity of the longest lived positron lifetime component, I_3, decreases.

This decrease might be explained by the motion of molecules of the polymer at the temperatures higher than about 150 K.

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